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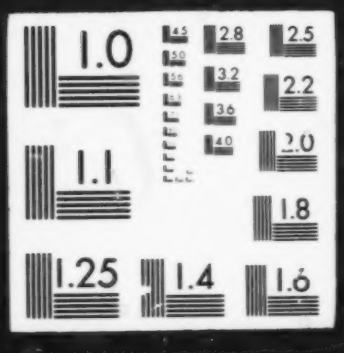

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ANALYSIS OF CYANIDE IN WATER AND WASTE SAMPLES

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Environmental Health Center
Cincinnati, Ohio

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ANALYSIS OF CYANIDE IN WATER AND WASTE SAMPLES

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for the

Standard Methods Committee of the
Federation of Sewage and Industrial Wastes Associations

ANALYSIS OF CYANIDE IN WATER AND WASTE SAMPLES

1.0 Introduction

The presence of cyanide in water has a significant effect upon the biological activity of the system. For example, Dodge and Reams[1] report that the threshold limit of toxicity at infinite time for fish appears to be at 0.1 mg/l as CN. Ludzack et al,[2] found that the microorganisms responsible for self-purification were inhibited by a CN content of 0.3 mg/l or above. The toxicity limits are affected by water quality, temperature, type and size of organisms, etc., hence definite limits are difficult to establish, but the figures quoted indicate the nature of effects due to cyanides in water.

Cyanides may exist in water in a variety of forms. The simple salts of sodium, potassium or ammonia are quite soluble and very toxic. Double salts or complex forms of cyanide show varying degrees of reactivity, depending upon the metal present and the type of compound. For example, a double salt of cadmium potassium cyanide reacts in the same manner as a simple cyanide with respect to analytical procedures. On the other hand, potassium cobalticyanide is quite stable and decomposes very slowly under similar conditions.

Most cyanide compounds are highly reactive. The analytical procedures used for their estimation are not specific; therefore the major problem is that of isolation from interferences. Although many procedures for the analysis of cyanide have been published, relatively few of these are satisfactory for general use in water and industrial waste analysis.

The following procedures were selected because they are applicable for many types of samples. The methods were found effective on relatively pure water, river water, sewage and several industrial wastes, including those from gas and coke operation, petroleum refining, and plating. The procedures described and recommended have been studied at the Environmental Health Center.(3)

1.1 Precautionary Measures - Due care should be exercised in manipulation of cyanide samples because of the toxicity involved. They should be processed in a hood or other well ventilated area. Avoid inhalation or ingestion of the sample or products of that sample. Do not attempt to acidity a sample unless liberated HCN can be trapped or controlled.

1.2 Preservation of Sample - Since most cyanides are very reactive and unstable, analysis should be made as soon as possible after sampling. If the sample cannot be analyzed immediately, add sodium hydroxide to raise the pH to 11.0 or above, and store in a cool place.

1.3 Interferences - Common interferences in the analysis for cyanide include the following: A. sulfides, B. heavy metal ions, C. fatty acids and other steam-distillable organic compounds, D. thiocyanates and cyanates, E. glycin, urea, or other substances which hydrolyze to form cyanides under analytical conditions, F, substances contributing color or turbidity, G. oxidizing agents. The first three affect the silver nitrate titration in an adverse

manner, D and E interfere in color development. F affects both the titration and colorimetric methods; G is likely to result in the destruction of cyanide during manipulation, particularly during the distillation stage.

1.4.0 Precision and Sensitivity:

1.4.1 The modified Liebig titration when used at a cyanide level above 1 mg/l as CN^- has a coefficient of variation* of 2.0 per cent for distilled samples or with relatively clear samples without significant interference. Extraction, removal of sulfides or oxidizing agents, tends to increase the variation to a degree determined by the amount of manipulation required and the type of sample. The limit of sensitivity is approximately 0.1 mg/l as CN^- but at this point the color change is indistinct. At 0.4 mg/l, the C. V. is four times that at a concentration level greater than of 1.0 mg/l as CN^-.

1.4.2 The pyridine-pyrazolone sensitivity data are given for a final volume of 25 ml after color development on the aqueous readings and in 10 ml of added solvent for extracted samples. The color was extracted from a 25 ml volume in order to compare data with the aqueous readings but no detectable difference in precision was obtained on extractions where 100 ml of sample was used.

	CV	Sensitivity(1)	Effective Range(2)
Aqueous color reading	4.8 per cent	0.5 μg	1-5 μg
Extracted color reading	3.9 per cent	0.1 μg	0.2 to 2.0 μg

* CV = 100 ($s/\bar{x}$); where s = sample standard deviation, $\bar{x}$ = mean.

(1) Sensitivity is defined as the amount of CN^- required to produce an absorbance of 0.05 or above with precision not more than twice the CV given.

(2) Effective range is the amount of CN^- in micrograms present in the reaction tubes (25 ml aqueous or 10 ml solvent) to result in an absorbance reading from 0.1 to 1.0

1.4.3 The sensitivity of the extracted sample is determined by the ratio of water to solvent volume. Greater sensitivity would be possible with a greater concentration factor than that used here (2.5) but since this represents 4 ppb of CN^-, greater ratios are not indicated. Primary advantage of extraction is in the greater precision. The figures given are for distilled samples. A turbid sample indicated approximately the same precision on the extracted sample with a large increase in variation for the aqueous reading.

1.4.4 The proposal by Serfass[5] that the titration apply for samples at a cyanide concentration greater than 1 mg/l as CN^- and the colorimetric test below this level has been substantiated by the sensitivity and precision of the two methods at the respective cyanide level indicated.

2.0 Removal of Interfering Substances

2.1 Sulfides are removed by treating the alkaline sample (pH > 11.0) with small increments of powdered lead carbonate and mixing. Black lead sulfide precipitates in samples containing sulfides. Repeat this operation until no more lead sulfide forms. Filter and rinse the precipitate, add the rinse-water to the filtrate, from which an aliquot may be used for analysis. Avoid a large excess of lead carbonate and a long time of contact in order to minimize complexation or occlusion of the cyanide with the precipitated material.

2.2 Fatty acids form soaps under alkaline titration conditions which render it difficult or impossible to detect the end point. This

type of interference may be removed by an extraction as suggested by Kruse and Mellon.[4] The sample should be acidified with acetic acid to pH 6.0 - 7.0 and extracted with isooctane, hexane or chloroform (preference in the order named). One extraction with a solvent volume equal to 20 per cent of the sample volume is usually adequate to reduce the fatty acids to a point below the interference level. Avoid multiple extractions or a long contact time at a low pH in order to keep the loss of HCN at a minimum.

2.3 Oxidizing agents are removed by use of the procedure outlined by Serfass et al.[5] If the sample indicates a positive test with starch iodide test paper, titrate with sodium sulfite (12.6 g anhydrous Na_2SO_3 per liter of solution) until a negative test is obtained.

2.4 After the removal of sulfides, fatty acids and oxidizing agents, if necessary, most other interferences can be removed by distillation. Two methods for the distillation of cyanide samples are presented, with the choice of method determined by the type of sample, the requirements of the analysis and availability of apparatus. The two methods selected are: A. the reflux procedure of Serfass et al,[5] B. Tartaric acid distillation as described by Ruchhoft et al.[6] The Serfass reflux method is preferable since it results in higher recovery of cyanide. The difference in recovery of cyanide is very small on those samples that are easily hydrolyzed, but the more stable the complex, the greater the difference in recovery between the two procedures. The apparatus and manipulation for the reflux procedure are somewhat more complicated than that with tartaric acid distillation.

2.4.A.0.0 Serfass Reflux Procedure(5)

A.1.0 Apparatus:

A.1.1 One liter Claissen boiling flask: $ joints

A.1.2 Air inlet: $ joint with a 3 mm i.d. glass tube fused to the joint and extended to 1/4 in of the bottom of flask A.1.1

A.1.3 Allihn type condenser: $ joint to fit A.1.1

A.1.4 Gas washer: spiral flow type, capacity of liquid 100 to 250 ml (such as the Fisher Milligan), preferably fitted with a drain tube in the bottom

A.1.5 Suction flask: 500 ml capacity

A.1.6 Water aspirator

A.1.7 Heating element (for A.1.1). Connecting tubing of rubber or glass as indicated.

A.2.0 Reagents. All reagents of A.R. grade dissolved in distilled water.

A.2.1 Sodium hydroxide: 4 g/100 ml of solution

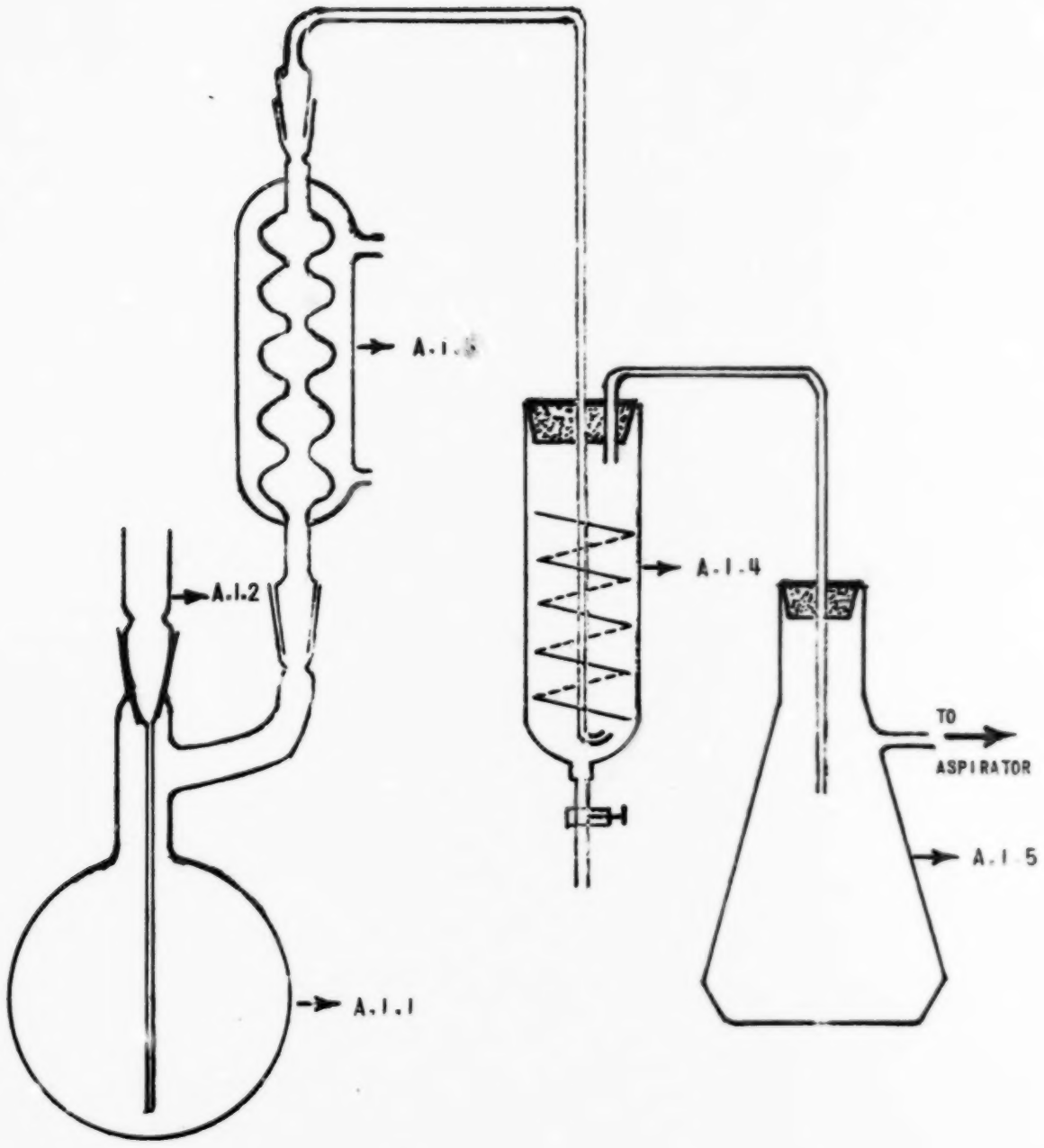
A.2.2 Mercuric chloride: 34 g/500 ml of solution

A.2.3 Magnesium chloride: 51 g $MgCl_2.6H_2O$/100 ml of solution

A.2.4 Sulfuric acid: concentrated

A.3.0 Procedure:

A.3.1 Add sample to A.1.1, diluted if necessary to between 250 and 500 ml with distilled water. Adjust condenser water flow to A.1.3. Add 50 ml of caustic (A.2.1) to the gas washer (A.1.4), and dilute if necessary with distilled water to adjust the volume to obtain



2.4.A.1.0 APPARATUS — SCHEMATIC OUTLINE

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an adequate depth of liquid in the absorber. Connect the train consisting of boiling flask air inlet, flask, condenser, gas washer, suction flask trap, and aspirator, with tubing. Start the water aspirator and adjust the suction so that approximately one bubble of air per second enters the boiling flask through the air inlet. This air rate will effectively act as a carrier for the HCN gas from flask to absorber but will not permit a reverse flow of HCN through the air inlet. If the air rate is too high the absorber will not trap all of the HCN.

A.3.2 Add 20 ml of mercuric chloride solution (A.2.2) and 10 ml of magnesium chloride (A.2.3) through the air inlet tube. Rinse the tube with distilled water and allow the air flow to mix the flask contents for two to three minutes. Slowly add 5 ml of concentrated sulfuric acid (A.2.4) and rinse the air inlet once more.

A.3.3 Heat at a rate which will provide rapid boiling but will not flood the condenser inlet or permit vapors to rise more than halfway into the condenser. Reflux for one hour. Turn off the heat but continue the air flow. After 15 minutes' cooling, drain the gas washer contents into a separate container. Rinse the connecting tube from the condenser to the gas washer, and the gas washer, with distilled water, add the rinse water to the drained liquid which may then be analyzed by titration or colorimetrically after dilution to a definite volume.

A.3.4 Refill the gas washer with a fresh charge of caustic and repeat step A.3.3

A.3.5 If the sample contains readily hydrolyzed cyanides, the first sample of absorber liquid will contain all of the available cyanide; if stable complex cyanides are present, a significant yield will appear in the second sample from the absorber or in several successive samples, depending upon the degree of stability.

2.4.B.0.0 Tartaric Acid Distillation

B.1.0 Apparatus:

B.1.1 One liter Pyrex distilling flask (Corning No. 3360 or equivalent)

B.1.2 Graham condenser: to fit B.1.1

B.1.3 Extension tube: attached to the condenser outlet to deliver the distillate well below the surface of the alkali in the receiver.

B.1.4 Receiving cylinder. 500 ml graduate cylinder or equivalent

B.1.5 pH meter. (See "pH Measurement," Sec. , p.)

B.2.0 Reagents: A.R. grade prepared in distilled water

B.2.1 Tartaric acid: 15 g/100 ml of solution

B.2.2 Sodium hydroxide: 2 g/100 ml of solution

B.2.3 Methyl orange indicator: 0.5 g/1000 ml of solution . This may be used in place of the pH meter (B.1.5).

B.3.0 Procedure:

B.3.1 Titrate a portion of the sample with tartaric acid (B.2.1) to approximately pH 5.0, or to a methyl orange end point. Record the volume of sample and acid required, then discard the aliquot used.

B.3.2 Add the volume of sample to be used for distillation to the boiling flask (B.1.1). If necessary, dilute the sample to 300 ml with distilled water. A few boiling chips should be added to prevent bumping.

B.3.3 Place 50 ml of caustic (B.2.2) in the receiving cylinder (B.1.4) and adjust the delivery tube from the condenser (B.1.3) so that it releases the distillate within 1/4 in of the bottom of the receiving cylinder or well below the surface of the caustic. Adjust the condenser cooling water.

B.3.4 On the basis of the preliminary titration with tartaric acid (B.3.1), calculate the volume of acid necessary to reduce the pH of the sample in the flask to 5.0 (approximate). Add this volume to the sample plus 5.0 ml of additional tartaric acid. Stopper the flask immediately and be sure that the joint between condenser and flask is tight.

B.3.5 Heat the contents to boiling and distill to the 250 ml mark in the receiving cylinder. The distillate plus caustic may then be mixed and analyzed for cyanide by the titration or colorimetric method.

B.3.6 The first 50 ml of distillate will contain nearly all of the cyanide which can be readily hydrolyzed. If the cyanide compound is stable, the distillation of the entire volume of sample might be insufficient for a high recovery of CN^-

3.0 Determination of Cyanide

3.1 The concentration of cyanide in the distilled sample may be determined by C, the modified Liebig titration[5, 6] using the rhodanine internal indicator of Ryan and Culshaw,[7] or by D, the pyridine-pyrazolone color test as outlined by Epstein.[8] On samples of unknown cyanide concentration, titrate 200 ml of the distilled sample, reserve the remaining 50 ml for the color test (3.D.0.0). The amount of sample to be used for titration or color test may be estimated from the data in Sec 1.4.0 on "Precision and Sensitivity."

3.C.0.0 Modified Liebig titration for cyanide:

C.1.0 Apparatus:

C.1.1 Koch microburette: 5 ml capacity

C.2.0 Reagents:

C.2.1 Silver nitrate 0.0192 N (3.27 g of $AgNO_3$/liter of solution in distilled water). Standardize this reagent against NaCl using the Mohr method with K_2CrO_4 indicator. Sec. , p. (1 ml $AgNO_3$ = 1 mg as CN^-).

C.2.2 Sodium hydroxide: reagents A.2.1 or B.2.2 may be used.

C.2.3 Indicator: p-dimethylaminobenzalrhodanine; 0.02 g/100 ml of acetone solution.

C.3.0 Procedure:

C.3.1 Take an aliquot of A.3.3 or B.3.5 without pH adjustment. If the sample has not been distilled, adjust the pH to 11.0 or above with sodium hydroxide reagent. Dilute the sample to 250 ml or some other convenient volume to be used for all titrations. Add 0.5 ml of indicator

(C.2.3). If the analyst has better results with more or less indicator as a result of visual sensitivity, the same amount of the selected volume should be used for all titrations. Titrate the sample with silver nitrate (C.2.1) to the first change in color from a canary yellow to salmon hue. Titrate a blank containing the same amount of alkali and water to obtain a correction for the sample titration.

Most analysts find this titration difficult for the first few titrations, as indicated by a high blank value. As the analyst becomes accustomed to the end point, blank titrations decrease to one crop or less and precision improves accordingly.

C.4.0 Calculations:

$$\frac{(A - B) \times 1000}{\text{ml original sample used}} \times \frac{250}{\text{aliq.}} = \text{ppm as } CN^-$$

A = ml sample titration with 0.0192 N $AgNO_3$

B = ml blank titration.

3.D.0.0 Colorimetric method for cyanide.

The pyridine-pyrazolone color test as proposed by Epstein[8] has been slightly modified to improve sensitivity and precision.

D.1.0 Apparatus:

D.1.1 Spectrophotometer or filter photometer: adjustable for absorbance[9] measurement at 620 or 630 millimicrons

D.1.2 Absorption cells: 1.0 cm corex preferred

D.1.3 Reaction tubes: A series of test tubes approximately 1 x 8" fitted with rubber stoppers.

D.2.0 Reagents:

D.2.1 Chloramine T: one per cent aqueous solution (prepared fresh daily)

D.2.2 1-phenyl-3-methyl-5-pyrazolone: Prepare a saturated aqueous solution (solubility approximately 0.5 g/100 ml) by adding the pyrazolone to water at approximately 75°C. Agitate occasionally as the solution cools to room temperature. If necessary, the pyrazolone (melting point 127-128°C) may be purified by recrystallization from ethanol. Usually this is not required.

D.2.3 Pyridine: A.R. grade

D.2.4 Bis-pyrazolone: (bis-1-phenyl-3-methyl-5-pyrazolone): Preparation: Dissolve 17.4 g of pyrazolone (D.2.2) in 100 ml of ethanol. Add 25 g of freshly distilled (under reduced pressure) phenylhydrazine. Reflux in an all-glass apparatus. Several hours of refluxing are necessary to produce the bis-pyrazolone which is indicated by formation of crystals in the reflux mixture. A reflux of 6-8 hours followed by standing at room temperature overnight, and 1-2 hours reflux the following day, is generally adequate for a good yield. Filter while hot, wash with hot ethanol (95 per cent) and air-dry. The product (melting point > 320°C) is stable indefinitely in dry form.

D.2.5 Mixed reagent: (prepare fresh daily). Mix 125 ml of a filtered, saturated solution of pyrazolone (D.2.2) with a filtered solution of 25 ml pyridine (D.2.3) containing 0.025 g of bis-pyrazolone (D.2.4) in solution (several minutes of mixing are usually necessary to dissolve D.2.4 in pyridine). The mixed reagent develops a pink color on standing but this does not affect the color production with cyanide if used within 24 hours.

D.2.6 Stock cyanide solution: 2.51 g KCN/l of solution in distilled water. Standardize against silver nitrate by the Liebig titration. The solution loses strength gradually and must be rechecked every week (approximate strength 1 ml = 1 mg as CN^-).

D.2.7 Standard cyanide solution: (prepare fresh at frequent intervals). Dilute 10 ml of D.2.6 to 1:1 with distilled water, mix and make a second dilution of 10 ml to 100 ml (1 ml = 1 microgram as CN^-, or 0.001 times the concentration of D.2.6)

D.2.8 N butyl alcohol. A.R. grade

D.2.9 Disodium phosphate solution. 5 g anhy. Na_2HPO_4/100 ml of solution

D.2.10 Acetic acid. 25 ml glacial acetic/100 ml of solution

D.3.0 Procedure:

D.3.1 An aliquot of the absorption liquid from distillation should be adjusted with acetic acid (D.2.10) to pH 6 to 7. Use a correction factor in the calculation of results if the volume change is significant.

D.3.2 Carefully rinse a set of reaction tubes and stoppers (D.1.3) with distilled water. Include a blank (all reagents, but without cyanide) standard, and a series of dilutions of the sample depending upon the cyanide concentration. Distilled water should be added if necessary to equate tube volumes. If extraction is to be used (D.3.7), this step makes it unnecessary to separate the two-phase system and adjust the solvent to a standard volume; the same fraction of the alcohol will dissolve in samples, standard and blank.

D.3.3 Add 0.2 ml of chloramine T (D.2.1), stopper and mix by inversion two or three times. Allow one to two minutes for the reaction.

D.3.4 Add 5.0 ml of mixed reagent (D.2.5), stopper and mix by inversion. Allow twenty minutes for color development.

D.3.5 If the aqueous color is to be measured, dilute all reaction tubes accurately to a selected volume (usually 25 ml), mix and read absorbance[9] at 620 millimicrons. If the color is too intense, repeat the test with a smaller aliquot.

D.3.6 Greater precision and sensitivity are possible if extracted color is used for the spectrophotometric reading (D.3.7)

D.3.7 At the end of the color development period in step D.3.4, add 1 ml of 5 per cent disodium phosphate (D.2.9) and the selected volume of carefully measured n-butyl alcohol (usually 10 ml) (D.2.8). Stopper and mix by inversion. If the emulsion formed by the two-phase system does not break within 1-3 minutes, add more of the phosphate and mix again. Withdraw an aliquot of the alcohol layer and measure the absorbance at 630 millimicrons.

D.4.0 Calculations: Parts per billion (ppb) as CN^- =

$$\frac{\text{Absorbance sample} \times 1000 \times A \times B \times C}{\text{Absorbance standard} \times (\text{ml sample for color test})}$$

A = micrograms CN^- in standard reaction tube

B = dilution factor in distillation =

$$\frac{\text{total ml absorption liquid}}{\text{ml original sample distilled}}$$

C = dilution factor for color development =

$$\frac{\text{ml sample diluted for color test}}{\text{ml of absorption liquid used}}$$

4.0 General Comments

4.1 The titration for cyanide can be adapted for high concentrations by increasing the strength of silver nitrate solution or by diluting the sample before distillation, after distillation, or both. It is advisable to adjust sample size or strength of silver nitrate so that the titration is from 2.0 to 10.0 ml.

4.2 The importance of distillation cannot be overemphasized. This step not only isolates cyanide from most interferences, but results in the conversion of most complex cyanides into simple compounds readily measured by titration or color test. The color test, in particular, is sensitive to buffer capacity of the sample. Although the pyridine-pyrazolone color reaction normally is reproducible through a pH range of 3.0 to 8.0, a significant buffer capacity definitely decreases the effective pH range. Therefore the distillation is necessary to isolate buffering components and reduce the various sample types to a basis comparable to that of the standard sample. The presence of sodium acetate due to neutralization of the alkali does not have a significant effect upon the color reaction.

4.3 All simple cyanides (type formula $M(CN)_x$ where M is a metal and x represents the number of CN groups), and the complex cyanides of zinc, cadmium, nickel and silver are easily distilled by either of the described procedures. Yield of added cyanide is generally in excess of 95 per cent, provided distillation is the only step required for removal of interference. Ferri- and ferro-cyanides require longer time, but either method of distillation will result in a high recovery of the com-

bined cyanide. In most cases complex copper cyanides require the Serfass distillation to effect a high quantitative recovery. Cobalticyanides were the most stable cyanide compounds encountered. Recovery was very low by tartaric acid distillation and in the range of 20 per cent of combined cyanide by the Serfass reflux method for two hours. When the refluxing was continued for 28 hours, cyanide was still being recovered.

4.4 The extraction of the pyridine-pyrazolone color may render it possible to avoid distillation in some cases. This procedure is similar to that of Nusbaum and Skupeko[10] and is very effective if turbidity is the principal interference. In such cases, the reliability of the test would be verified if the same results were obtained with and without distillation.

4.5 The pyridine-pyrazolone color will not develop in a quantitative manner in the alcohol layer or if the phosphate is added before the color development is essentially complete in the aqueous phase.

4.6 In all cases, it is advisable to express the results in terms of CN^- because all cyanide must exist at some transitory stage as CN^- in order to be measured. "Free cyanide" is an arbitrary term that may include simple cyanides and a variable proportion of complex cyanides, depending upon the stability of the complex. "Total cyanide" is also a misnomer, as cobalticyanides, for example, do not release all of the combined cyanide in any practical time schedule with the methods as applied at this time.

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